Synthesis of Polyaniline and Its Derivatives

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Synthesis of Polyaniline and Its Derivatives

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Chapter 1. Introduction

Conducting polymers (CPs) are an important class of optoelectronic materials. The light weight, mechanical flexibility, thermal and chemical stability, and simple processing, as well as the designable properties of these materials may significantly improve optoelectronic device efficiency and manufacturing processes. Poly(*para*-phenylene), polyfluorene, polypyrrole, polythiophene, polyaniline, poly(phenylene ethynylene), and poly(phenylene vinylene) are all representative CPs and some are currently at a practical application stage in light-emitting diodes, plastic lasers, solar cells, field-effect transistors, and sensors. Many methods for the synthesis of CPs including chemical oxidative polymerization, electrochemical polymerization, and organometallic polycondensation have been reported. However, it is difficult to control the polydispersity, molecular weight, and the end groups of the CPs. Since CPs are typically synthesized through step-growth mechanisms, the polydispersity index (PDI) of step-growth polymerization is predicted to be 2.0 when the monomer conversion is 100%. In order to design and synthesize CPs with desired functions, factors related to not only the electronic properties of the π-conjugated systems but also the structural characteristics such as the regioregularity and polydispersity are important because these structural qualities determine the aggregation morphology, and thus, affect the bulk properties. Thus, new design of monomers and new polymerization technique must be explored.

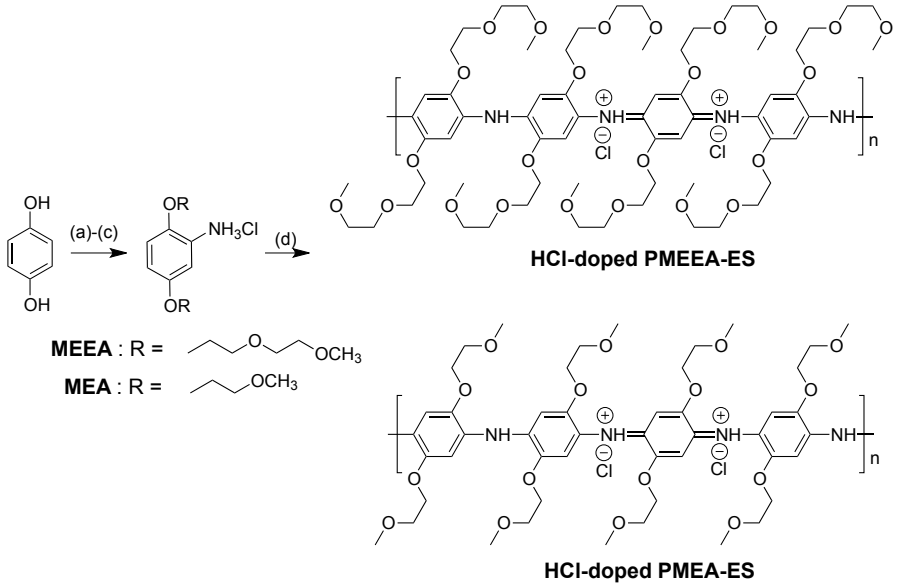
In my Ph D thesis, we focused on the synthesis of polyaniline (PANI) and its derivatives due to their ease of synthesis, good environmental stability, and unique reversible acid/base doping/dedoping process. Since PANI is basically insoluble in common solvents, in chapter 2, by the introduction of two hydrophilic substituents at 2,5-positions of the aniline moiety (2,5-dimethoxyethoxyaniline, MEA; 2,5-dimehoxyethoxyethoyaniline, MEEA), the highly water-soluble polyaniline derivative, PMEEA-ES (emeraldine salt) was synthesized. Moreover, HCl-doped PMEA-ES and PMEEA-ES showed good solubility in common organic solvents. Basically, polyaniline was prepared by the electrochemical or chemical oxidation of aniline. Under such conditions, the electronic structures of resulting polyanilines are very complicated since each polymer chain has different electronic structure depending on how many quinonoid rings it contains (namely, how much oxidant was used). In order to prepare polyaniline with a simply electronic structure, in chapter 3, we synthesized poly(3,9-carbazole) by metal-catalyzed polymerization of a new designed carbazole derivative. In chapter 4, we developed a new method for the synthesis of PANI with low polydispersity (1.3) by using a supramolecular ionic assembly comprised of anionic oligophenylene ethynylene (OPE) and anilinium cations, which is regarded as the reaction media. We propose that anilinium monomers form contact ion

pairs with the anionic OPE backbone and are locally concentrated along the ionic assembly; such a situation eventually enables the facilitation of the polymerization reaction and would suppress side reactions.

Chapter 2. Soluble Polyaniline Synthesized from 2,5-Substituted Anilines

Polyaniline, one of the important conducting polymers, has attracted considerable interest due to its potential applications in the fields of electronic devices, such as organic photovoltaics, sensors, and anti-corrosion coating. For such applications, it is better for materials to be soluble or melt-processable. Polyaniline is basically insoluble in water and common organic solvents, although it was found to be partially soluble in *N*-methylpyrrolidinone (NMP) and dimethylformamide (DMF). Thus, many investigations have been carried out to improve the solubility of PANI in common solvents through the polymerization of aniline derivatives with alkyl, alkoxy, benzyl, and aryl substituents at the aromatic ring or nitrogen. Recently, it has been reported that water-soluble PANI can be synthesized either by using functional acids as dopants or by introducing hydrophilic substituents onto the PANI backbone. The water solubility of those polyanilines was reported to be less than 100 g/L and such water-soluble polymers are generally scarcely soluble in common organic solvents.

In this chapter, we describe that a simple modification of anilines enables to prepare soluble PANIs. We designed aniline derivatives, MEEA and MEA, where hydrophilic 2-(2-methoxyethoxy)ethoxy and 2-methoxyetoxy moieties are introduced at 2,5-positions of aniline, respectively; we expected these substituents would help the resultant PANIs soluble in water and organic solvents (Scheme 1). In addition, the substitution at 2,5-position has advantage in terms of regioregularity of PANIs. For the synthesis of MEEA, firstly hydrophilic 2-(2-methoxyethoxy)ethoxy groups were introduced onto 1,4-hydroquinone. After the nitration reaction, the nitro group was reduced using Pd/C as a catalyst. The target compound, MEEA, was obtained as light yellow oil.



Scheme 1. Synthetic scheme for MEEA•HCl, MEA•HCl, HCl-doped PMEEA-ES, and HCl-doped PMEA-ES. Reagents and conditions: a) 2-(2-methoxyethoxy)ethoxy-*p*-toluenesulfonate for MEEA, K_2CO_3, toluene (refluxed, 48 h); b) Acetic acid, nitric acid, H_2O (25°C, 3 h); c) Pd/C, H_2, methanol (25°C, 12 h); d) Ammonium persulfate (APS), H_2O (pH = 2.5, adjusted with HCl) (25°C, 24 h).

We synthesized PANIs by a chemical oxidation of aniline derivatives with ammonium persulfate (APS) in H_2O (pH = 2.5) for 24h. When we used MEEA•HCl as a monomer, a deep green solution without any precipitates was obtained (Fig 1). The UV-VIS-NIR spectra of the reaction mixture are shown in Figure 1a. We observed the absorption

bands appeared at 288, 370 (sh), and 479 nm; the former two absorptions are attributed to the emraldine structure of PANI and a peak wavelength of 479 nm corresponds to polaron band of ES salt of poly(2,5-dialkoxyaniline), clearly showing the formation of HCl-doped poly-MEEA (HCl-doped PMEEA-ES). In addition, it was observed that a steadily increasing absorption starts from ~800 nm up to the near-IR region, which is characteristic of conductive PANIs. In fact, HCl-doped PMEEA-ES and HCl-doped PMEA-ES showed the similar conductivity in the range of 10^{-3} S/cm. The λ_{max} in VIS-NIR for HCl-doped PMEEA-ES and HCl-doped PMEA-ES appeared around at 1900 and 2100 nm, respectively, which consistent with the view that these polyanilines adopt an extended structure in their main-chain conformation in H_2O. When HCl-doped PMEEA-ES was solidified or dissolved into chloroform, however, these λ_{max} shifted to around 1000 nm or 1400 nm, respectively, indicating that the extended structure was turned into a folded structure in solid state and in organic solvents.

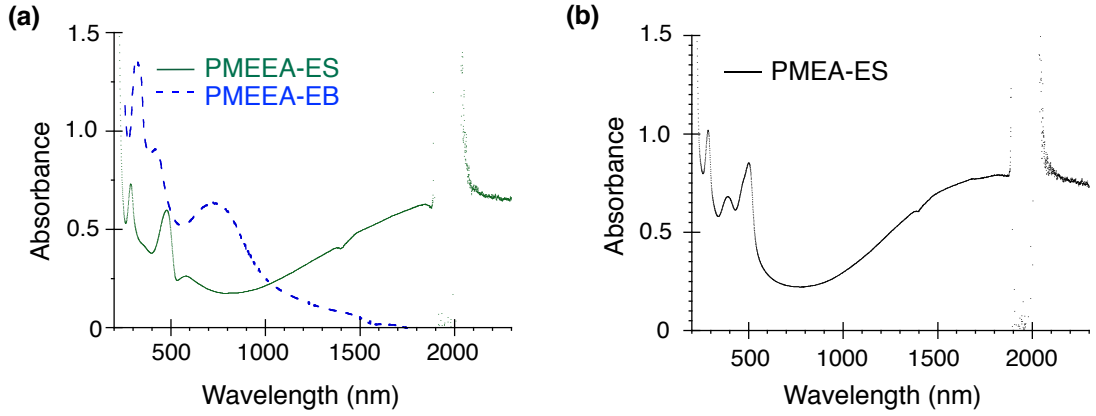


Figure 1. (a) UV-VIS-NIR spectra of HCl-doped PMEA-ES in H_2O and (b) HCl-doped PMEEA-ES (solid curve) and PMEEA-EB (suspension; dashed curve) in H_2O (lower) ($[PMEA]_{unit} = [PMEEA]_{unit} = 0.25$ mM, pH = 2.5, l = 1 mm.

Interestingly, both of HCl-doped PMMEA-ES and PMEA-ES showed high solubility in most of polar solvents (Table 1), such as NMP, dimethylsufoxide (DMSO), DMF, and methanol (MeOH), because the two hydrophilic side chains dramatically improved their solubility. PMEEA-ES can be dissolved in other polar solvent, such as tetrahydrofurane (THF, 40g /L), chloroform ($CHCl_3$, 40 g/L), acetone (50g /L), and acetonitrile (CH_3CN, 100g /L). Moreover, it showed unprecedented high solubility (400 g/L) in H_2O. As far as we know, the solubility of 400g/L in water is the highest value among polyanilines reported so far. Since the PMEEA-ES can be processed from a variety of polar and nonpolar organic solvents and water, it should be useful for simple manufactureing of multi-layered functional polymeric devices.

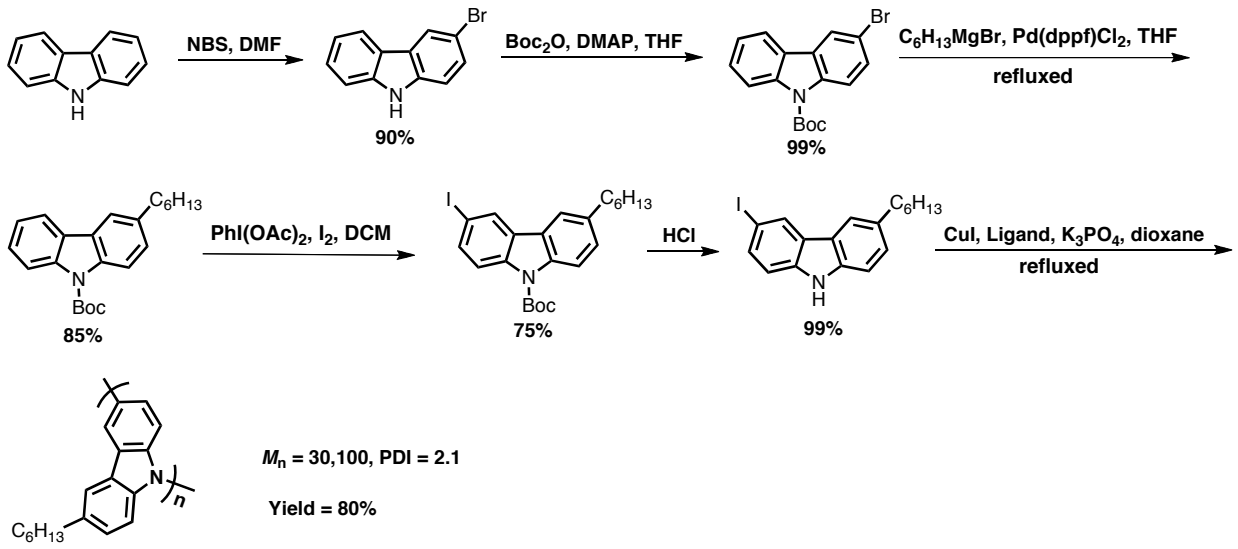
Table 1. Solubility of PMEEA and PMEA in various solvents[a]

Polymer	Solvents								
	H_2O	DMSO	THF	$CHCl_3$	DMF	Acetone	NMP	MeOH	MeCN
PMEEA-ES	HS	HS	S	S	S	S	S	S	S
PMEEA-EB	I	S	I	S	S	I	S	S	S
PMEA-ES	I	S	SS	PS	S	SS	S	S	PS
PMEA-EB	I	SS	I	I	I	I	S	I	I

[a]HS = highly soluble (400 g/L), stable for 1 month; S = soluble up to 1.0 g/L, stable for 1 month; PS = partially soluble under 1.0g/L, no precipitation within 1 week, but precipitation by centrifugation at 6000 rpm for 10 min. SS = slightly soluble under 1.0g/L, precipitation after 1 day, with a colored supernatant; I = insoluble

Chapter 3. Revisiting poly(3,9-carbazole): one of the regioisomers of polycarbazole featuring polyaniline backbone

In general, PANI is synthesized through the chemical or electrochemical oxidation of aniline, which produces, in most cases, insoluble materials because of not only the lack of solubilizing groups but also the structural defects such as cross-links. Poly(3,9-carbazole) [poly(3,9-Cz)] is an intriguing conjugated polymer due to the conjugation involving the lone pairs of carbazole's nitrogen like PANI. In 1988, poly(3,9-Cz) was first synthesized from 3,6-diiodocarbazole through Ullmann coupling; the authors indeed mentioned "In essence this polymer could be described as an annealed polyaniline." and examined the doping process of the polymer by spectroscopic methods. However, the ambiguities in the characterization of the polymer were remained both structurally and electronically because the monomer had two reactive iodo-groups. In 2002, poly(3,9-Cz) was synthesized from 3-iodocarbazole through the similar Ullmann conditions with the number average molecular weight (Mn) of 2,400. Absorption and fluorescence spectral data, and ionization potential of the polymer were reported; however, the authors mainly focused on oligomeric derivatives rather than the poly(3,9-Cz). Except these several examples, poly(3,9-Cz)s have attracted little attention in comparison with other regioisomers, although several 3,9-linked carbazole-based polymers such as copolymers and dendrimers have been reported. We therefore would like to revisit poly(3,9-Cz) through synthesizing a new monomer and applying the amination chemistry instead of Ullmann coupling (Scheme 2). The old and yet scarcely studied polymer was synthesized and fully characterized, and electronic characteristics of the polymer are investigated.



Scheme 2. Synthetic scheme for 3-hexyl-6-iodocarbazole and poly(3,9-Cz).

We designed 3-iodo-6-hexyl-carbazole (**3-1**) as a monomer; the hexyl chains can not only endow the polymer with solubility but also protect the redox active 6-position, which distinguish the present study from the abovementioned previous literatures. The monomer was synthesized through 5 steps of well-established reactions in 56% total yield from carbazole, which could provide gram quantities of the monomer. Polymerization was performed under Buchwald's *N*-arylation conditions using a copper catalyst. Poly(**3-1**) was purified through reprecipitation and obtained as brown powder. GPC analysis using polystyrene standard revealed the M_n of 30,100. ^{1}H NMR spectra of the monomer and poly(**3-1**) clearly evidenced the head-to-tail regioregular structure of the resultant poly(**3-1**) (Figure 2). When we carried out the polymerization under the Ullman conditions, we obtained Poly(**3-1**) with the Mn of 5,600 in a yield of 10%.

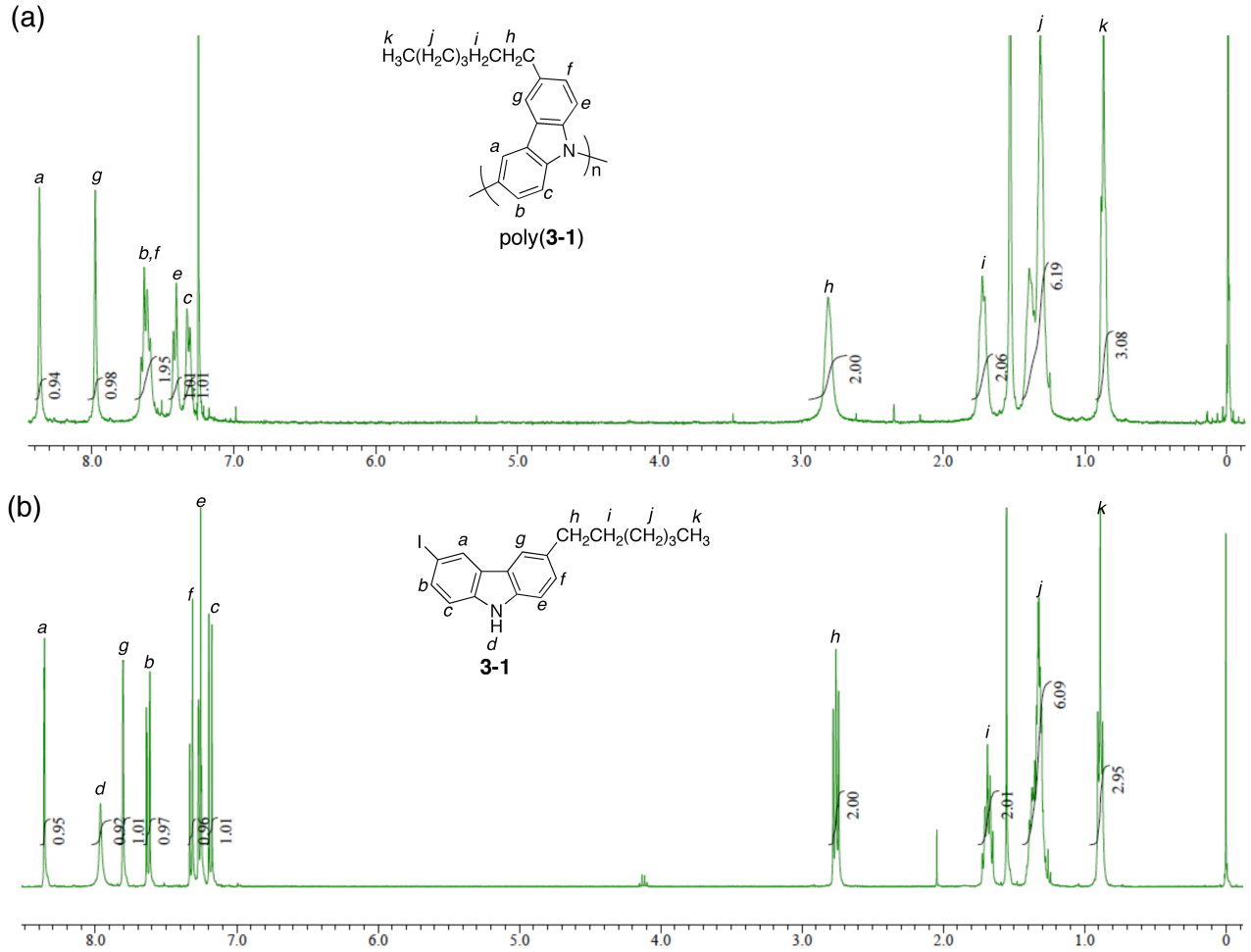


Figure 2. ^{1}H NMR spectra of (a) poly(**3-1**) and (b) **3-1** in $CDCl_3$.

Figure 3a depicts the cyclic voltammogram (CV) curve of poly(**3-1**) in CH_2Cl_2 with tetra-*n*-butylammonium perchlorate ($TBNPF_6$) as a supporting electrolyte using Ag/Ag^+ as a reference electrode (note that the potential hereafter is referenced to the Fc/Fc^+ couple). Poly(**3-1**) was oxidized at 0.52 V and reduced at 0.41 V in the first scan. In addition, we could observe that the electrochemical oxidation process of poly(**3-1**) is reversible, which indicates that the polymer is electrochemically stable. Taking advantage of the fact that the electrochemical oxidation process of poly(**3-1**) is reversible, we could perform UV-Vis-NIR spectral measurements for the electrochemical oxidized poly(**3-1**). With $TBNPF_6$ as a supporting electrolyte using Ag/Ag^+ as a reference electrode (note that the potential hereafter is referenced to the Fc/Fc^+ couple), the UV-Vis-NIR spectra of oxidized poly(**3-1**) film on an indium tin oxide (ITO) substrate in the solution of $TBNPF_6$ (0.1 mol L^{-1}) in acetonitrile were shown in Figure 3b. There is no spectral change under the oxidation potential of 0.68 V, which indicates that poly(**3-1**) cannot be oxidized under such low potential. However, we could observe the significant spectral changes in the near-IR region at 0.73 V, and the gradual increase of absorbance in near-IR region upon increasing the oxidation potential from 0.73 V to 0.88 V. Meanwhile, the color of poly(**3-1**) film was changed from white to deep blue. The broad absorption appeared in the near-IR region, which is characteristic of the conductive PANIs. This further approved that oxidized poly(3,9-Cz) featured the conducting form of PANI backbone (PANI-ES). When we continued to increase the oxidation potential to 1.08 V, no significant spectral change was observed. It should be noted that the oxidation potential observed here is different from CV result, probably due to that we use acetonitrile here instead of dichloromethane for CV measurement.

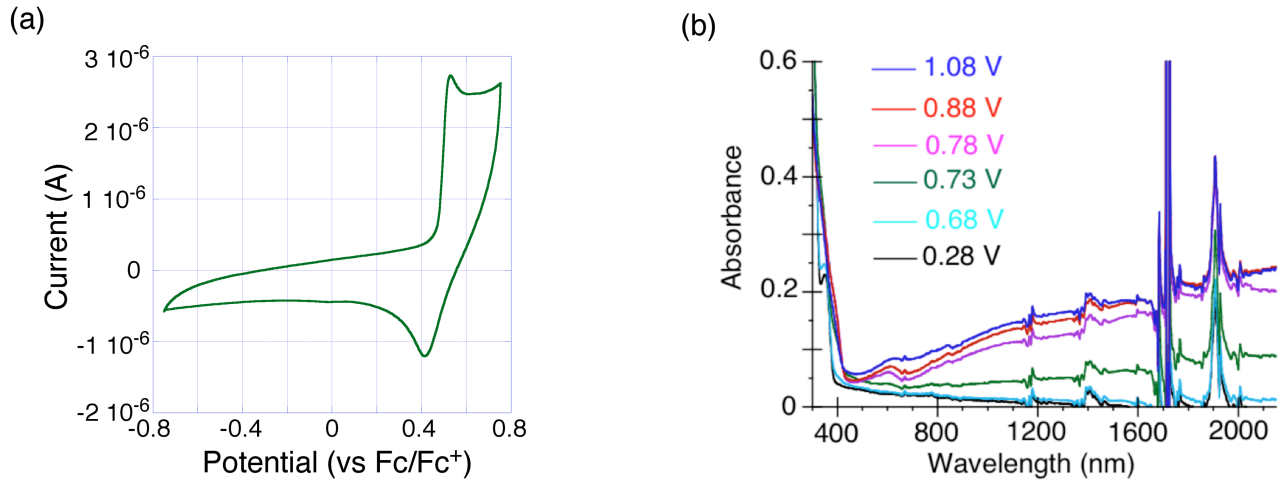


Figure 3. (a) Cyclic voltammograms of poly(**3-1**) ([**3-1**] = 0.01 mol L^{-1}) in CH_2Cl_2 in the presence of tetra-*n*-butylammonium perchlorate (0.1 mol L^{-1}) as supporting electrolyte with consecutive scans at 100 mV s^{-1} versus Ag/Ag. The first scan of three scans was shown here for clarity. (b) Absorption spectral changes of poly(**3-1**) film on an indium tin oxide (ITO) substrate in a solution of $TBNPF_6$ in acetonitrile (0.1 mol L^{-1}) induced upon increasing the oxidation potential. The poly(**3-1**) film was prepared by dropping the solution of poly(**3-1**) in THF on an ITO substrate and the solvent was evaporated slowly at room temperature.

We successfully synthesized poly(3,9-Cz) through designing a new monomer and applying *N*-arylation reaction to the polymerization. The polymer is highly soluble, electrochemically stable, and conducting in the doped state. Application of this old and yet new polymer in organic electronics, for example, as hole transport and electrochromic materials, is now underway in our laboratory.

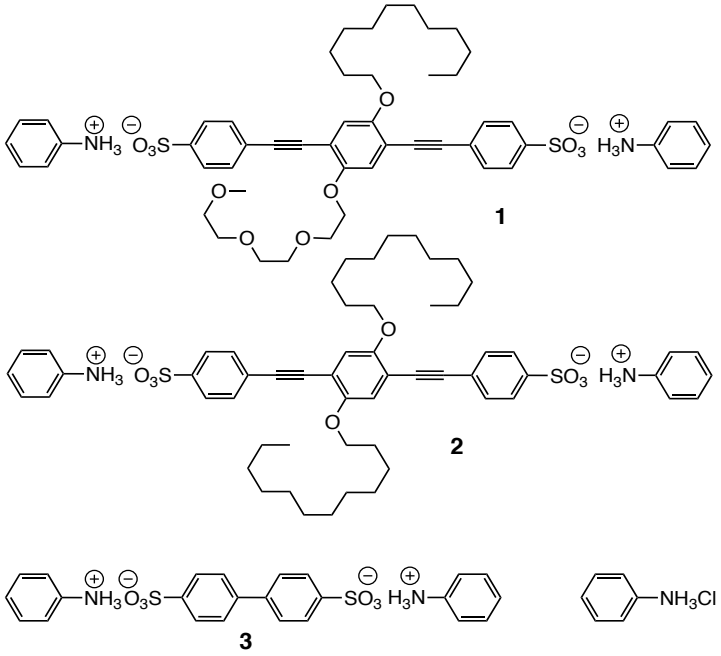
Chapter 4. Synthesis of PANI with low polydispersity using supramolecular ionic assembly as the reaction media

In order to design and synthesize CPs with desired functions, factors related to not only the electronic properties of the π-conjugated systems but also the structural characteristics such as the regioregularity and polydispersity are important because these structural qualities determine the aggregation morphology, and thus, affect the bulk properties.

Recently new polymerization techniques for CPs have been reported. In 2004, the groups led by Yokozawa and McCullough independently reported that a nickel-catalyzed coupling reaction of 3-alkylthiophene-based monomers proceeded in chain-growth manner, giving regioregular poly(3-alkylthiophene)s with a PDI close to 1. Recent development of this method has further enabled the controlled polymerization of other CPs such as polyphenylenes and polyfluorenes. In addition, Yu and Turner have succeeded in ring-opening metathesis polymerization (ROMP) of [2.2]paracyclophanedienes, which afforded soluble poly(phenylene vinylene)s with a PDI of 1.2. Accordingly, the chain-growth polymerization of CPs has opened new doors in synthetic polymer chemistry and organic electronics. However, in principle, the concept cannot be applied to the polymerization of aniline because it proceeds through the oxidative coupling of anilinium salts. Recently, Lo and Sleiman reported nucleobase-templated synthesis of poly(phenylene ethynylene)s. Importantly, the PDI values of the daughter polymer (i.e., poly(phenylene ethynylene)) were close to 1, copying that of the template polymer in spite of the step-growth nature of Sonogashira coupling polymerization. Furthermore, other templating approaches using porous coordination polymers (PCPs) and block copolymer micelles were found to be effective. In such unique reaction media, the propagation reaction occurred

preferentially against other side reactions and achieved a low PDI value. However, examples of conjugated polymer synthesis are still limited.

Inspired by the development of these templating approaches, we decided to pursue synthesis of PANI with a low PDI value since PANI is one of the remaining CPs for which such a polymerization has not yet been established. It should be noted that template-assisted polymerization of aniline has widely been examined so far, however, the previous researches focused on creating nanostructures of PANI replicating the template structures, and characterization of the polymer including PDI values has not been performed in detail. In Chapter 4, we describe supramolecular ionic assembly composed of anionic π-conjugated backbone and anilinium cations could provide unique polymerization media, where anilinium cations are concentrated and aligned. Remarkably, oxidative polymerization of aniline using the supramolecular template yielded PANI with PDI value as low as 1.3 (M_n = 20,500).



Scheme 3. Structures of compounds 1, 2, and 3. Anilinium chloride was used for comparison.

We designed and synthesized oligo(phenylene ethynylene) (OPE)-based anionic molecules, which have anilinium cations not only as counter ions but also as monomers (Scheme 3). To tune the balance between hydrophobicity and hydrophilicity of the molecules, which is essential for self-assembly in water, we introduced triethylene glycol and dodecyl chains in **1** and two dodecyl chains in **2**. Compound **3** was prepared for control experiments, which is analogous to **1** and **2** but does not assemble in water due to its compact structure. We prepared supramolecular assembly by dissolving **1** in water under sonication and then keeping the solution at 5°C. Figure 4a shows a SEM image for the freeze-dried sample of supramolecular assembly of **1** ([**1**] = 0.2 mM, pH = 2.5). We observed rectangular structures with a width of about 200–400 nm. The size of the supramolecular assembly in solution was also evaluated by using DLS. As shown in Figure 4b, the average size was about 300-500 nm, which is consistent with that observed in SEM observation. Compound **2** ([**2**] = 0.2 mM) was too hydrophobic and could not be dissolved in water. In contrast, composite **3** ([**3**] = 0.2 mM) was soluble but did not form any supramolecular assembly at all.

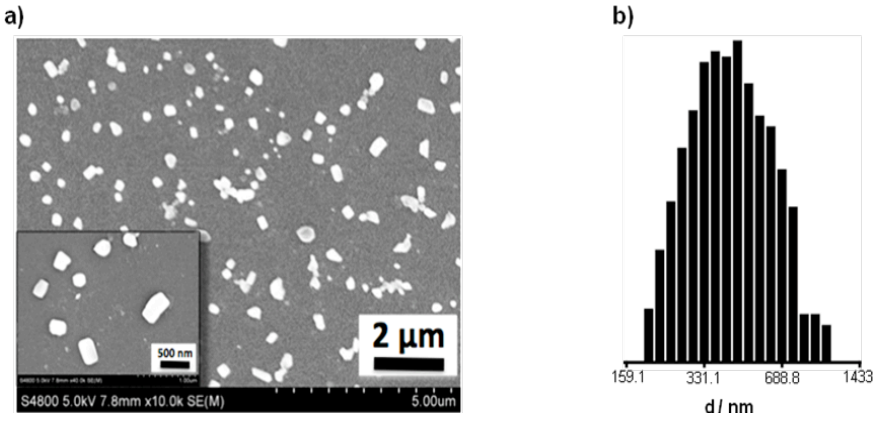


Figure 4. (a) A SEM image of the freeze-dried sample of 1 prepared in water: [1] = 0.2 mM, pH = 2.5. Inset shows an enlarged view of (a). (b) DLS profile of supramolecular assembly of **1** prepared in water: [**1**] = 0.2 mM, pH = 2.5.

Figure 5 displays variable-temperature (VT) absorption spectra of supramolecular assembly of 1. With lowering temperature form a molecularly dissolved solution of **1** at 75 °C, the red-shift in the π–π* transition of OPE in **1** from 362 to 368 nm with isosbestic points was observed along with a new shoulder band at 399 nm, which indicates the formation of supramolecular assembly of OPE chromophores at 5 °C.

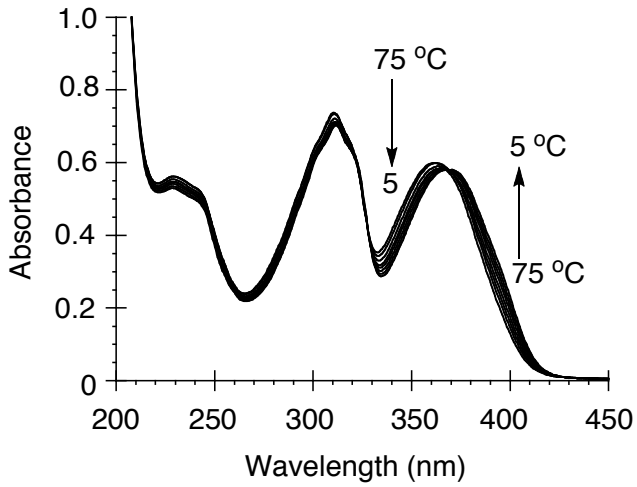


Figure 5. VT-UV absorption spectral changes of supramolecular assembly of 1 in water: [**1**] = 0.2 mM, pH = 2.5, *l* = 1 mm, cooled from 75°C to 5°C.

We also conducted VT-^{1}H NMR measurements of the supramolecular assembly of **1**. Figure 6a shows partial ^{1}H NMR spectra of **1**, wherein below 45°C, the proton signals of OPE backbone became broad, indicating the formation of supramolecular assembly. Importantly, the shift in proton signals of anilinium cation in **1** was scarcely observed during this process; in contrast, the chemical shifts of those in anilinium chloride and compound **3** moved to a lower magnetic field upon cooling. The change in the chemical shifts against the temperature is rationalized by the hydration-induced shift of free anilinium cations. These results in turn suggest that within the anionic supramolecular assembly of **1**, anilinium monomers would form contact ion-pair with anionic OPE backbone. Therefore, supramolecular assembly of **1** provides anilinium monomers with different surroundings from those in the bulk solution. We expect that oxidative polymerization of aniline in such a unique reaction media could be controlled.

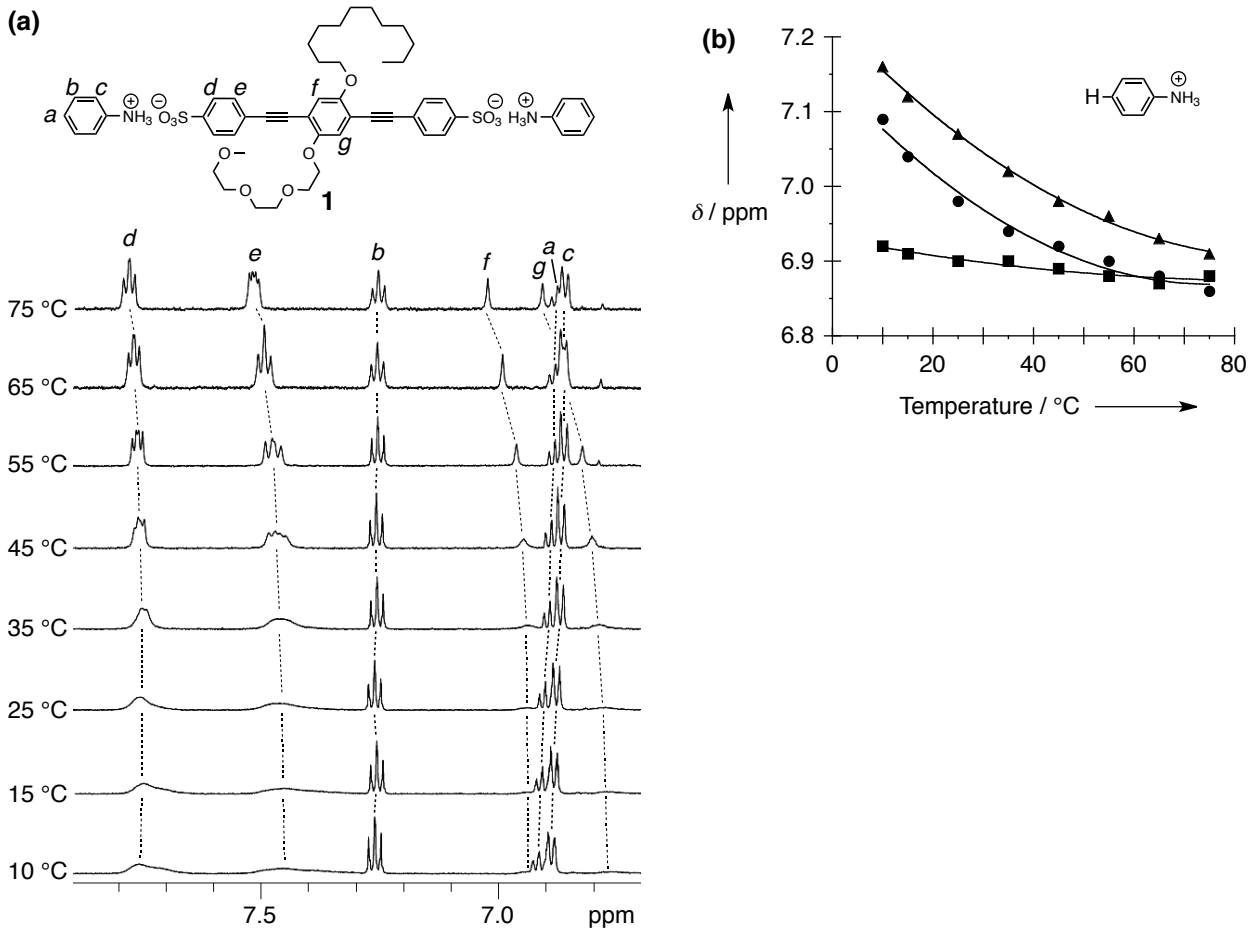


Figure 6. (a) VT-^{1}H NMR spectral changes of supramolecular assembly of **1** in water ([2,2,3,3-D_4] sodium 3-3-(trimethylsilyl) propanoate was used as an internal standard): [**1**] = 0.2 mM, pD = 2.5. (b) Plots of the chemical shifts of *p*-H in anilinium salts against temperature: anilinium chloride (solid triangle, [anilinium chloride] = 0.4 mM, pD = 2.5), compound **3** (solid dot, [**3**] = 0.2 mM, pD = 2.5), and compound **1** (solid rectangle).

With the above information in mind, we conducted oxidative polymerization of aniline. Absorption spectrum of the resultant solution showed an absorption maximum at 777 nm (1.6 eV), which is attributable to emeraldine salt form of PANI (namely, PANI-ES) (Figure 7a). Importantly, neither anilinium chloride nor compound **3** could be polymerized under the same conditions probably due to the low monomer concentration and temperature ([anilinium cation] = 0.4 mM, 0-5 °C, pH = 2.5). We infer that the supramolecular template can locally concentrate the monomers and facilitate the polymerization. Addition of potassium hydroxide solution basified the resultant solution and dedoped the PANI-ES, transforming PANI-ES into emeraldine base form (PANI-EB), which showed absorption maximum at 563 nm (2.2 eV). Then PANI-EB was precipitated out by adding dimethylformamide (DMF), filtered, and washed with methanol and water, and freeze-dried (yield 85%). Anionic template was readily isolated from the filtrate by evaporating solvents and can be re-used for further synthesis of polyaniline. A gel permeation chromatography (GPC) profile of the obtained PANI-EB is shown in Figure 7b. Remarkably, the polydispersity of our PANI-EB was narrow with a PDI of about 1.3 (Mn = 20,500, calculated using polystyrene standards).

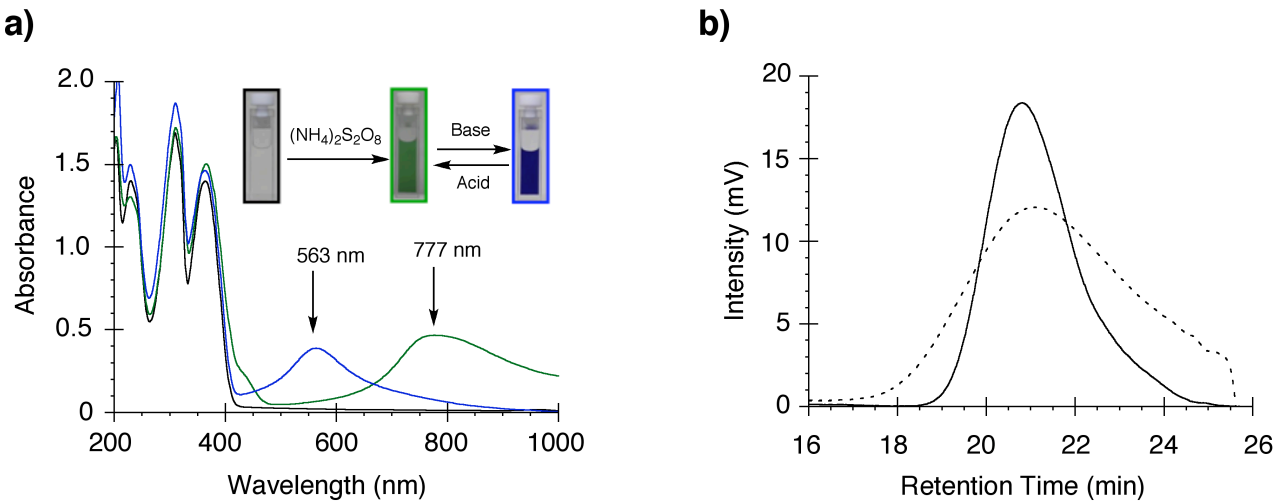


Figure 7. (a) Absorption spectra of PANI-ES (green line) and PANI-EB (blue line) obtained through the templating approach by: PANI-ES and EB were diluted from 1 mL to 4 mL by addition of H_2O (3 mL), l = 1 cm.(b) GPC profiles of (a) PANI-EB obtained through the templating approach (solid line) and commercially available PANI-EBs (dotted line: PDI (M_w): 1.8 (20,000)).

As the M_n and the structural quality of CPs profoundly influence the electrical properties, we measured the conductivity of the PANI-ES obtained from the supramolecular ionic assembly of **1**. PANI-ES films were prepared from PANI-EB (PDI = 1.3, M_n = 20,500) by doping with camphorsulfonic acid (CAS) in *meta*-cresol; this sample was drop-casted onto a silicon wafer. We measured the electrical conductivity of the PANI-ES film to be 190 S/cm at 25 °C using a four-terminal technique. In contrast, the conductivity of the commercially available sample, doped by the same procedure, was evaluated to be 28 S/cm (its GPC is shown in Figure 7b). In the case for PANI, it was reported that there is a relationship between the M_n and the electrical conductivity; our system would contribute to reveal the correlation between the PDI of PANI and the electrical conductivity.

Chapter 5. Conclusion

In conclusion, we successfully synthesized soluble PANIs derivatives, such as HCl-doped PMEA-ES and PMEEA-ES by a simple modification of anilines upon the introduction of hydrophilic group at 2,5-position of aniline. The HCl-doped PMEEA-ES exhibited unprecedentedly high water solubility of 400 g/L and moderate solubility (1 g/L) for a variety of common organic solvents, such as DMSO, chloroform, acetone, THF, MeCN, and MeOH. Interestingly, PMEEA in the EB state can also be dissolved into MeCN and chloroform. In addition, we revisited poly(3,9-Cz) through designing a new monomer and applying *N*-arylation reaction to the polymerization. The polymer is highly soluble and electrochemically stable. We also developed the new synthetic strategy for PANI with low PDI using a supramolecular ionic assembly as a reaction medium. In our case, within a supramolecular ionic assembly, anilinium monomers form contact ion pairs with the anionic OPE backbone and are locally concentrated. Such a situation eventually enables the facilitation of the polymerization reaction and would suppress side reactions. The conductivity of the PANI-EB doped with CAS in meta-cresol was estimated to be 190 S/cm, which was higher than commercially available PANI, suggesting that structural qualities determine the aggregation morphology, and thus, affect the bulk properties. We successfully demonstrated this approach is applicable to several anilinium cations to give PANIs with low PDI.